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Citation: The Journal of Chemical Physics **120**, 5664 (2004); doi: 10.1063/1.1650296
View online: http://dx.doi.org/10.1063/1.1650296
View Table of Contents: http://aip.scitation.org/toc/jcp/120/12
Published by the American Institute of Physics

Mixing rules for multicomponent mixture mass diffusion coefficients and thermal diffusion factors

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(Received 13 November 2003; accepted 2 January 2004)

Mixing rules are derived for mass diffusion coefficient and thermal diffusion factor matrices by developing compatibility conditions between the fluid mixture equations obtained from nonequilibrium thermodynamics and Grad's 13-moment kinetic theory. The mixing rules are shown to be in terms of the species mole fractions and binary processes. In particular, the thermal diffusion factors for binary mixtures obtained by the Chapman–Enskog expansion procedure are suitably generalized for many-component mixtures. Some practical aspects of the results are discussed including the utilization of these mixing rules for high pressure situations. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1650296]

I. INTRODUCTION

Thermal diffusion factors become important at high pressures[1] or high temperatures.[2,3] In a review of multicomponent diffusion, Curtis and Bird[4] discuss mixing rules for mass diffusion matrices from the combined perspectives of the thermodynamics of irreversible processes and dilute gas kinetic theory (KT), providing a means of generalizing relations between fluxes and driving forces. However, the discussion of thermal diffusion processes and associated matrices in Ref. 4 is limited, without explicit generalized mixing rules for thermal diffusion factor matrices. The lack of such rules, needed to adequately model thermal diffusion processes, hinders appropriate multicomponent calculations of high temperature phenomena, such as combustion. In the context of approximations based on KT rather than generalized mixing rules, some examples of applications involving multicomponent mixture calculations that focus on the Soret effect are chemically frozen boundary layers, chemical vapor deposition, chemical reactions, vapor condensation and evaporation[2] and also studies of flame structures for burning methane or hydrogen.[5,6] However, at high pressures, accepted mixing rules do not exist for either mass diffusion or thermal diffusion, although thermal conductivity and viscosity mixing rules have been documented in the literature.[7] High-pressure phenomena are of great interest in explaining the physics of the gaseous planets, of extraction processes, of liquid rocket propulsion and of diesel engines. The primary goal of this investigation is to inquire about the structural form of the mass and thermal diffusion matrices and provide associated mixing rules. Also of interest are arguments that may guide the utilization of these mixing rules under high pressure situations.

General equations for fluid mixtures applicable to vapors, liquids and the supercritical region, may be obtained through the formalism of nonequilibrium thermodynamics (NEQT).[1,8,9] Because the NEQT equations are of general validity, it is desirable to use them rather than those of KT in problems where the thermodynamic variables may vary over a wide range. However, the NEQT formalism does not provide transport coefficient models; these must be obtained by other means, such as KT for dilute to moderately dense gases. Two KT forms exist. The Chapman–Enskog procedure[10] involves complex expansions in terms of the inverse density (i.e., the mean free path) for calculating the transport properties. The 13-moment theory of Grad[11,12] is however, much simpler in that it involves a single expansion in terms of velocities and it is therefore preferred here. The essential idea for deriving mixing rule matrices is that the conjunction of NEQT and KT should provide a needed starting point for such formulation. This conjunction is a necessary condition for any general theory because it must converge to the KT in the low pressure regime.

This paper is organized as follows: First, the 13-moment theory is recalled in Sec. II and presented in a convenient form for comparison with NEQT theory, which is briefly described next in Sec. III. The NEQT theory is then considered for low pressure situations, so that it describes the physics within the same space of thermodynamic values as the KT. Then, substituting the 13-moment transport formulas into the NEQT forms results in a coupled set of matrix equations that relate the mixture mass and thermal diffusion coefficients to binary diffusion coefficients; these equations represent the compatibility conditions, derived in Sec. IV. These compatibility conditions lead to the mixing rules in Sec. V, both for mass diffusion coefficients and thermal diffusion factors matrices. For the thermal diffusion factors, these mixing rule consists of expressions for the mixture thermal diffusion factors (flux cross-couplings) in terms of binary factors and thermal conductivities; these expressions are functions of the binary mass and heat diffusion coefficients as well. The results are forms that are convenient, so that appropriate approximations may be judiciously applied. The paper is concluded with a discussion in Sec. VI that covers the practical applications of the results and emphasizes the possible utilization of the mixing rules at high pressure situations. The generalization of the Chapman and Cowling[10] thermal diffusion factors is a major aspect of this study.

II. THE THIRTEEN-MOMENT THEORY

There are two ways to express Grad's 13-moment equations:[11] the theoretically basic manner is as functions of the collision integrals, and the application-focused manner is in terms of the species transport coefficients, which has greater flexibility. Because the present emphasis is on applications, the latter manner is chosen, to the extent possible. In writing the equations, the interest is fluid behavior at times much longer than the characteristic collision times and spatial gradient scales that are much larger than the mean free path. This allows coupling between tensor properties differing by one order to be neglected, as required by the principles of NEQT.[8,13] The result is the ''normal,'' otherwise known as the continuum form of the equations, which are utilized here.

For a mixture of N species, $1 \leqslant i \leqslant N$, the coupling between mass and heat fluxes by the 13-moment method is given by[11,12]

$$\sum_{j=1}^{N} \frac{1}{X_j}\left(K_{ij}^{MM}\mathbf{J}_j + \frac{1}{R_u T} K_{ij}^{MQ}\mathbf{q}_j'' \right) = -n\overline{D}_i\left[\nabla \ln X_i + \left(1 - \frac{m_i}{m}\right)\nabla \ln p \right] \tag{1}$$

$$\sum_{j=1}^{N} \frac{1}{X_j}\left[K_{ij}^{QQ}\mathbf{q}_j'' + (R_u T) K_{ij}^{QM}\mathbf{J}_j \right] = -\lambda_i \nabla T, \tag{2}$$

where X_j is the molar fraction of species j, K_{ij} represents KT coupling matrices, $\mathbf{J}_i$ is the molar flux of species i, R_u is the universal gas constant, T is the temperature, $\mathbf{q}_i''$ is the Bearman–Kirkwood (BK) heat flux[14] of species i, n is the molar density, $\overline{D}_i \equiv (\Sigma_{j\neq i} X_j / D_{ij})^{-1}$ is Blanc's law diffusivity calculated from the D_{ij}'s which are the KT first approximation to the binary mass diffusivity, m_i is the molar weight of species i, $m = \Sigma_{i=1}^{N} m_i X_i$ is the mixture molar weight, p is the pressure, and λ_i is the KT thermal conductivity for species i; superscripts M and Q are associated with mass and heat, respectively. The coupling matrices K are expressed in terms of collision integral ratios that are defined by other ratios, A_{ij}^*, B_{ij}^*, and C_{ij}^*, as given by Hirshfelder *et al.*,[13]

$$\varkappa_{ij} \equiv \tfrac{11}{2} - \tfrac{8}{5}A_{ij}^* - \tfrac{6}{5}B_{ij}^*, \tag{3}$$

$$\zeta_{ij} \equiv \tfrac{6}{5}C_{ij}^* - 1, \tag{4}$$

where the ratios are functions of the normalized temperature $T^* \equiv kT/\epsilon_{ij}$, with ϵ_{ij} being the characteristic molecular interaction potential. Physically, $\varkappa_{ij}$ are associated with the species cross-coupling of the heat fluxes, while ζ_{ij} are proportional to the binary thermal diffusion factors[13] and have values much less than unity. For the Lennard-Jones 6–12 potentials, $\varkappa_{ij}$ varies very weakly with T^* having values between 2.2–2.43, while $\zeta_{ij} \leqslant 0.14$, and $|\zeta_{ij}| \leqslant O(10^{-2})$ for $T^* < 1$. The coupling matrices can now be expressed in terms of these ratios as

$$K_{ij}^{MM} = \delta_{ij} - (1-\delta_{ij})\frac{\overline{D}_i X_j}{D_{ij}}, \tag{5}$$

$$K_{ij}^{MQ} = \delta_{ij}\overline{D}_i \sum_{k\neq i} \frac{m_k}{m_i + m_k}\frac{X_k \zeta_{ik}}{D_{ik}} - (1-\delta_{ij})\frac{m_i}{m_i + m_j}\frac{\overline{D}_i X_j \zeta_{ij}}{D_{ij}}, \tag{6}$$

$$K_{ij}^{QQ} = \delta_{ij} - (1-\delta_{ij})\frac{m_i m_j}{(m_i + m_j)^2}\frac{\overline{D}_i X_j \varkappa_{ij}}{D_{ij}}\mathrm{Le}_i, \tag{7}$$

$$K_{ij}^{QM} = \frac{5}{2}\mathrm{Le}_i \overline{D}_i\left[\delta_{ij}\sum_{k\neq i}\frac{m_k}{m_i + m_k}\frac{X_k \zeta_{ik}}{D_{ik}} - (1-\delta_{ij})\frac{m_j}{m_i + m_j}\frac{X_j \zeta_{ij}}{D_{ij}} \right], \tag{8}$$

where

$$\mathrm{Le}_i \equiv \frac{\gamma_i - 1}{\gamma_i}\frac{\lambda_i}{R_u n \overline{D}_i} \tag{9}$$

is a species i Lewis number and γ_i is the specific heat ratio of species i. For the 13-moment method $\gamma_i = 5/3$. Following the results of Harstad,[12] Le_i is given in terms of the collision integrals in Appendix A.

III. NONEQUILIBRIUM THERMODYNAMICS FORMULATION

In KT, individual heat fluxes are one of the inherent results of the derivation. In NEQT, the individual fluxes are not typically utilized. The endeavor of bridging the gap between NEQT and KT prompts us to utilize the individual heat fluxes $\mathbf{q}_i''$ as the departure point for developing the formalism that will allow expressing the NEQT transport coefficients in terms of the KT ones. The generalized mass and heat transport equations are[1]

$$\mathbf{J}_i = -n\left[X_i(D_{T,i}\nabla \ln T + D_{p,i}\nabla \ln p) + \sum_{k=1}^{N-1} \mathcal{D}_{ik}\nabla X_k \right], \tag{10}$$

$$\mathbf{q}_i'' = -X_i\left[\lambda_i''\nabla T + nR_u T\left(D_{p,i}''\nabla \ln p + \sum_{k=1}^{N-1} \mathcal{D}_{ik}''\nabla X_k \right) \right], \tag{11}$$

where λ_i'' is the BK thermal conductivity, $D_{T,i}$ is a form of the thermal diffusion ratio embodying the Soret effect, $D_{p,i}$ is the pressure diffusion ratio, $\mathcal{D}_{ik}$ are the molar mixture diffusivities, $D_{p,i}''$ are the pressure-gradient diffusivities, $\mathcal{D}_{ik}''$ are the diffusivities associated with the Dufour effect. The superscript $(\,)''$ is here used to denote transport properties associated with the BK heat fluxes, $\mathbf{q}_i''$ and $\mathbf{q}''$; quantities without $(\,)''$ are associated with the molar fluxes. Conventionally

$$\mathbf{q}'' = \sum_{i=1}^{N} \mathbf{q}_i'' = -\lambda''\nabla T - nR_u T\left(D_p''\nabla \ln p + \sum_{k=1}^{N-1} \mathcal{D}_{Qk}''\nabla X_k \right), \tag{12}$$

where

$$\lambda'' = \sum_{i=1}^{N} X_i \lambda_i'' \tag{13}$$

is the mixture BK thermal conductivity and

$$D_p'' = \sum_{i=1}^{N} X_i D_{p,i}'', \tag{14}$$

$$\mathcal{D}_{Qk}'' = \sum_{i=1}^{N} X_i \mathcal{D}_{ik}'', \tag{15}$$

are mixture quantities equivalent to the corresponding species quantities. In typical NEQT theory, the quantities λ_i'', $D_{p,i}''$, and $\mathcal{D}_{ik}''$ are undefined, and instead only the quantities λ'', D_p'', and $\mathcal{D}_{Qk}''$ are utilized in the fluxes. The goal of this study is to determine λ'', D_p'', and $\mathcal{D}_{Qk}''$ from comparison of the NEQT and KT.

Further manipulations of the NEQT transport coefficients involves expressing them in terms of the mass diffusion factor matrix

$$\alpha_{D,ij} \equiv X_i \frac{1}{R_u T} \frac{\partial \mu_i}{\partial X_j},$$

where μ_i is the chemical potential of species i, along with a symmetric (with null diagonal) mass diffusion matrix D_m and an antisymmetric BK thermal diffusion factor matrix α_T.[1,8,9] The following expressions are then obtained for individual species:

$$D_{T,i} = \sum_{j=1}^{N} Y_j \alpha_{T,ij} D_{m,ij}, \tag{16}$$

$$D_{p,i} = \frac{p}{R_u T} \sum_{j=1}^{N} Y_j \frac{m_i m_j}{m} \left(\frac{v_i}{m_i} - \frac{v_j}{m_j} \right) D_{m,ij}, \tag{17}$$

$$\mathcal{D}_{ik} = \sum_{j=1}^{N} D_{m,ij} \frac{m_j}{m} (Y_j \alpha_{D,ik} - Y_i \alpha_{D,jk}), \tag{18}$$

and for the mixture

$$\lambda'' = \lambda + n R_u \sum_{\substack{i>j \\ j \in [1,N-1]}} X_i X_j (\alpha_{T,ij})^2 D_{m,ij}, \tag{19}$$

$$D_p'' = \frac{mp}{R_u T} \sum_{\substack{i>j \\ j \in [1,N-1]}} Y_i Y_j \alpha_{T,ij} \left(\frac{v_i}{m_i} - \frac{v_j}{m_j} \right) D_{m,ij} = \frac{p}{R_u T} \sum_{j=1}^{N} X_j v_j D_{T,j}, \tag{20}$$

where also

$$\mathcal{D}_{Qk}'' = \sum_{\substack{i>j \\ j \in [1,N-1]}} \alpha_{T,ij} (Y_j \alpha_{D,ik} - Y_i \alpha_{D,jk}) D_{m,ij} = \sum_{j=1}^{N} D_{T,j} \alpha_{D,jk}, \tag{21}$$

where $Y_i = m_i X_i / m$ is the mass fraction of species i, $v_i = \partial v / \partial X_i = \partial \mu_i / \partial p$ are the partial molar volumes and $\Sigma_{i=1}^{N} Y_i D_{T,i} = 0$, $\Sigma_{i=1}^{N} Y_i D_{p,i} = 0$, and $\Sigma_{i=1}^{N} m_i \mathcal{D}_{ik} = 0$. The advantage of the representation embodied in Eqs. (16)–(21) is that the determination of coefficients in Eqs. (10) and (12) is now replaced with obtaining mixing rule expressions for matrices D_m (for $N=2$, $D_{m,12}$ is the binary diffusivity) and α_T which are unavailable in NEQT but available in KT. This task will be accomplished in Sec. V based on the compatibility conditions determined in Sec. IV.

An alternate, simplified form of the diffusion matrix is

$$\mathcal{D}_{ik} = \sum_{j=1}^{N} D_{ij}^M \alpha_{D,jk}, \tag{22}$$

where

$$D_{ij}^M \equiv D_i^* \delta_{ij} - (1 - \delta_{ij}) D_{ij}', \tag{23}$$

$$D_{ij}' \equiv Y_i \frac{m_j}{m} D_{m,ij}, \tag{24}$$

$$D_i^* \equiv \sum_{j=1}^{N} \frac{m_j}{m_i} D_{ji}', \tag{25}$$

with the following relationships applying: $X_i D_{ji}^M = X_j D_{ij}^M$, $\Sigma_{i=1}^{N} m_i D_{ij}^M = 0$, $\Sigma_{j=1}^{N} D_{ij}^M Y_j = 0$.

Equations (10)–(25) are valid in the entire thermodynamic regime. To compare NEQT to KT, the low p perfect gas limit of the NEQT is taken. For low-pressure perfect gases described by KT, $pv_i = R_u T$ leading to $\alpha_{D,ij} = \delta_{ij} - \delta_{iN}$, where for convenience the major component of the mixture is chosen to be N. Further manipulations lead to

$$\mathcal{D}_{ik} = D_{ik}^M - D_{iN}^M, \tag{26}$$

$$D_{T,i} = \frac{m}{m_i} \sum_{j=1}^{N} \alpha_{T,ij} D_{ji}', \tag{27}$$

$$D_{p,i} = \sum_{j=1}^{N} \left(\frac{m_j}{m_i} - 1 \right) D_{ji}', \tag{28}$$

$$D_p'' = \sum_{j=1}^{N} X_j D_{T,j}, \tag{29}$$

$$\mathcal{D}_{Q,k}'' = D_{T,k} - D_{T,N}. \tag{30}$$

IV. COMPATIBILITY CONDITIONS

The compatibility conditions are found by substituting Eqs. (1) and (2) into Eqs. (10) and (11), respectively, assuming that $\nabla \ln T$, $\nabla \ln p$, and ∇X_k for $k \neq N$ are independent and nulling their coefficients in each of the relationships obtained for the molar and heat fluxes. The known quantities are the binary mass diffusion and binary thermal diffusion coefficients and the purpose of these compatibility relations is to derive mixing rules in order to calculate the mixture mass diffusion and thermal diffusion coefficients as functions of the (assumed known) binary ones and of the thermodynamic properties. Thus, the following relationships are obtained:

$$\lambda_i'' = \sum_{j=1}^{N} (K^{QQ})_{ij}^{-1} \lambda_j - n R_u \left(\sum_{j=1}^{N} F_{ij} D_{T,j} + \phi_i^T \right), \tag{31}$$

$$D''_{p,i}=\phi_i^p-\sum_{j=1}^{N} F_{ij}D_{p,j}, \tag{32}$$

$$\mathcal{D}''_{ik}=\phi_i^k-\phi_i^N-\sum_{j=1}^{N}\frac{F_{ij}\mathcal{D}_{jk}}{X_j}, \tag{33}$$

$$\sum_{j=1}^{N} G_{ij}D_{T,j}=\sum_{j=1}^{N} K_{ij}^{MQ}\phi_j^T-\frac{1}{nR_u}\times\sum_{j,k=1}^{N} K_{ij}^{MQ}(K^{QQ})_{jk}^{-1}\lambda_k, \tag{34}$$

$$\sum_{j=1}^{N} G_{ij}D_{p,j}=\left(1-\frac{m_i}{m}\right)\overline{D}_i-\sum_{j=1}^{N} K_{ij}^{MQ}\phi_j^p, \tag{35}$$

$$\sum_{j=1}^{N} G_{ij}\frac{D_{jk}^M}{X_j}=\overline{D}_i\left(\frac{\delta_{ik}}{X_i}-\psi_i\right)-\sum_{j=1}^{N} K_{ij}^{MQ}\phi_j^k, \tag{36}$$

where

$$\mathsf{G}\equiv\mathsf{K}^{MM}-\mathsf{K}^{MQ}\mathsf{F},\quad \mathsf{F}=(\mathsf{K}^{QQ})^{-1}\mathsf{K}^{QM}, \tag{37}$$

and the ϕ_i's and ψ_i are arbitrary functions satisfying $\Sigma_{i=1}^{N}X_i\phi_i=0$ and $\Sigma_{i=1}^{N}X_i\psi_i=1$. Through K^{QM}, F is associated with the thermal diffusion factors (Dufour effect). The functions ϕ_i only affect individual species heat fluxes $\mathbf{q}''_i$, but not the total flux $\mathbf{q}''$. Since the net mass flux is null, only $N-1$ of Eq. (36) is independent.

V. MIXING RULES

The mixing rules must relate the known KT transport properties to those of the NEQT, which are unknown. What is desired is to calculate $\alpha_{T,ij}$ and D_{ij}^M as functions of binary processes and some thermodynamic variables.

A. Preliminary calculations

The initial focus is on heat flux compatibility. To fruitfully compare the heat fluxes from KT and NEQT, the heat flux must be expressed in terms of a mixture thermal conductivity, λ, whose relationship to the λ_j's must be found. Examining Eq. (2) it is clear that an inverse of K^{QQ} in that equation must be taken to express $\mathbf{q}''_i$ as a function of λ_i and ultimately of λ. Such an inverse indeed exists because $\mathrm{Le}_i=O(1)$ and

$$\varkappa'_{ij}\equiv m_im_j\varkappa_{ij}/(m_i+m_j)^2 \tag{38}$$

with $\varkappa'_{ij}\lesssim 3/5$, so that matrix K^{QQ} given by Eq. (7) is diagonally dominant and thus invertible. Therefore

$$\mathbf{q}''_i=-X_i\left[\nabla T\sum_{j=1}^{N}\lambda_j(K^{QQ})_{ij}^{-1}+R_uT\sum_{j=1}^{N}F_{ij}\frac{\mathbf{J}_j}{X_j}\right] \tag{39}$$

and the total BK heat flux is

$$\mathbf{q}''=\sum_i\mathbf{q}''_i=-\lambda\nabla T-R_uT\sum_{i,j=1}^{N}F_{ij}\mathbf{J}_j\frac{X_i}{X_j}, \tag{40}$$

where

$$\lambda=\sum_{i,j=1}^{N}\lambda_jX_i(K^{QQ})_{ij}^{-1} \tag{41}$$

is the mixture thermal conductivity.

Because the compatibility conditions involve $(\mathsf{K}^{QQ})^{-1}$, this quantity must be first found in order to examine the consequences of Eqs. (31)–(36). To this purpose, a new diffusion coefficient characterizing heat transfer is introduced, D_{ij}^Q, such that

$$(K^{QQ})_{ij}^{-1}=\Lambda_i\left[\delta_{ij}+(1-\delta_{ij})\mathrm{Le}_i\frac{\overline{D}_iX_j}{D_{ij}^Q}\right], \tag{42}$$

where

$$\Lambda_i^{-1}=1-w_i\sum_{j\neq i}^{N}w_j\frac{\varkappa'_{ij}}{D_{ij}D_{ij}^Q}, \tag{43}$$

$$w_j\equiv\mathrm{Le}_j\overline{D}_jX_j, \tag{44}$$

where $\varkappa'_{ij}$ is defined by Eq. (38) and the symmetry condition $\Lambda_i/D_{ij}^Q=\Lambda_j/D_{ji}^Q$ holds. For $N=2$ and $N=3$, explicit expressions for D^Q can be calculated and are given in Appendix B. For larger N, such expressions are not readily found and an approximation must be then considered. The idea is to use series expansions to calculate D^Q. To this end, two matrices U and N are defined by

$$U_{ij}\equiv\frac{(1-\delta_{ij})}{D_{ij}^Q}\quad\text{and}\quad N_{ij}\equiv\frac{(1-\delta_{ij})\varkappa'_{ij}}{D_{ij}}, \tag{45}$$

which according to Eqs. (7) and (42) are related by

$$N_{ij}=U_{ij}-\sum_{k=1}^{N}U_{ik}w_kN_{kj} \tag{46}$$

and an expansion for U is formally proposed

$$\mathsf{U}=\sum_{n=1}^{\infty}\mathsf{U}^{(n)}, \tag{47}$$

where

$$\mathsf{U}^{(1)}=\mathsf{N}, \tag{48}$$

$$U_{ij}^{(n)}=(1-\delta_{ij})\sum_{k=1}^{N}U_{ik}^{(n-1)}w_kN_{kj}\quad\text{for } n>1. \tag{49}$$

By truncating the U series, an approximation for D^Q can be found. Owing to limitations in the accuracy of both D_{ij} and $\varkappa_{ij}$, which are given by KT collision integrals, for practical calculations, at most two decimal place accuracy is needed for U.

A weighting factor for the conductivity mixing rules, w_i^Q, is defined by

$$X_iw_i^Q\equiv\sum_{j=1}^{N}X_j(K^{QQ})_{ji}^{-1}, \tag{50}$$

which can be calculated from D^Q through

$$w_i^Q=\Lambda_i\left(1+\sum_{\substack{j=1\\ j\neq i}}^{N}\frac{w_j}{D_{ij}^Q}\right) \tag{51}$$

which according to Eq. (41) enables the calculation of the thermal conductivity $\lambda=\Sigma_{i=1}^{N}X_iw_i^Q\lambda_i$. Note that w_i^Q corresponds to the Wassiljewa-type weighting that is frequently

used for mixture thermal conductivities.[7] For $N=2$ and $N=3$, explicit expressions for w_i^Q are given in Appendix B.

Moreover, w_i^Q enables the calculation of a weighting factor, w_i^T, for the thermal diffusion factors. Because only the total heat flux is considered in practical applications, according to KT, an effective binary thermal diffusion ratio can be defined through

$$X_j\overline{\alpha}_{T,j}^b \equiv \sum_{i=1}^{N} X_i F_{ij} \tag{52}$$

which is best expressed in terms of binary thermal diffusion factors

$$\overline{\alpha}_{T,i}^b = \sum_{\substack{j=1 \\ j\neq i}}^{N} X_j \alpha_{T,ji}^b, \tag{53}$$

where according to Eqs. (42), (51), and (52),

$$\alpha_{T,ij}^b = \zeta_{ij}\frac{(m_i w_j^T - m_j w_i^T)}{(m_i+m_j)D_{ij}}, \tag{54}$$

where we define

$$w_i^T \equiv \frac{5}{2}\mathrm{Le}_i\overline{D}_i w_i^Q = \frac{w_i^Q \lambda_i}{R_u n}. \tag{55}$$

Although unlike in appearance, for $N=2$, $\alpha_{T,12}^b$ is algebraically equivalent to the binary thermal diffusion factors of Chapman and Cowling[10] obtained from the Chapman–Enskog procedure. That is, $\alpha_{T,ji}^b$ may be regarded as the appropriate generalization of the binary thermal diffusion factors for multicomponent mixtures; similarly, w_i^T are the appropriate generalization of the weighting factors determining the binary thermal diffusion factor matrix.

B. Mixing rule determination

1. Thermal diffusion

To obtain the mixing rule for the thermal diffusion factors, we combine Eqs. (33), (52), and (53) which leads to

$$\mathcal{D}''_{Q,k} = \sum_{i,j=1}^{N} X_i \alpha_{T,ji}^b \mathcal{D}_{jk}, \tag{56}$$

where α_T^b is the binary KT thermal diffusion factor matrix. Utilizing Eqs. (26) and (30) in Eq. (56) results in

$$D_{T,j} = \sum_{i,m=1}^{N} X_m\left(\frac{m_i}{m_j}\alpha_{T,jm}^b - \alpha_{T,im}^b\right)D'_{ij}. \tag{57}$$

But since Eq. (27) is also valid, this implies that the mixture thermal diffusion factor matrix α_T is simply a linear combination of the binary matrix α_T^b, that is

$$\alpha_{T,ij} = \sum_{m=1}^{N} X_m\left(\frac{m_j}{m}\alpha_{T,im}^b - \frac{m_i}{m}\alpha_{T,jm}^b\right) \tag{58}$$

leading to the desired mixing rule

$$\alpha_{T,ij} = \frac{m_i}{m}\overline{\alpha}_{T,j}^b - \frac{m_j}{m}\overline{\alpha}_{T,i}^b. \tag{59}$$

To verify that Eq. (59) indeed satisfies Eqs. (31)–(33), which are related to the heat flux, we first combine Eqs. (32), (52), and (53) to obtain

$$D''_p = \sum_{j,m=1}^{N} X_j X_m \alpha_{T,jm}^b D_{p,j} \tag{60}$$

and use Eq. (28) to further calculate

$$D''_p = \sum_{i,j,m=1}^{N} X_j X_m\left(\frac{m_i}{m_j}\alpha_{T,jm}^b - \alpha_{T,jm}^b\right)D'_{ij}. \tag{61}$$

On the other hand Eqs. (29) and (57) can be combined to yield

$$D''_p = \sum_{i,j,m=1}^{N} X_j X_m\left(\frac{m_i}{m_j}\alpha_{T,jm}^b - \alpha_{T,im}^b\right)D'_{ij} \tag{62}$$

which means that Eqs. (61) and (62) are equivalent if

$$\sum_{i,j,m=1}^{N} X_j X_m(\alpha_{T,jm}^b - \alpha_{T,im}^b)D'_{ij} = 0 \tag{63}$$

or using Eq. (53) to transform Eq. (63) the equivalence, if true, is stated by

$$\sum_{i,j=1}^{N} X_i X_j(\overline{\alpha}_{T,i}^b - \overline{\alpha}_{T,j}^b)\frac{m_i m_j}{m^2}D_{m,ij} = 0. \tag{64}$$

The statement of Eq. (64) is clearly correct since the terms in the sum are antisymmetric in i and j. Thus, the mixing rule for the pressure terms in the heat flux is verified.

To verify the mixing rule for the thermal conductivity part of the heat flux, we combine Eqs. (31) and (52) to obtain

$$\lambda'' = \lambda - nR_u\sum_{j=1}^{N} X_j\overline{\alpha}_{T,j}^b D_{T,j}. \tag{65}$$

Using Eq. (16) in Eq. (65) to replace $D_{T,j}$ leads to

$$\lambda'' = \lambda + nR_u\sum_{i,j=1}^{N}\frac{m_i}{m}X_i X_j\overline{\alpha}_{T,j}^b\alpha_{T,ij}D_{m,ij} \tag{66}$$

which is equivalent to Eq. (19) if

$$\sum_{i,j=1}^{N}\left(\frac{m_i}{m}\overline{\alpha}_{T,j}^b - \frac{1}{2}\alpha_{T,ij}\right)X_i X_j\alpha_{T,ij}D_{m,ij} = 0. \tag{67}$$

Using Eq. (59) to transform the expression in the parentheses leads to $0.5\times((m_i/m)\overline{\alpha}_{T,j}^b + (m_j/m)\overline{\alpha}_{T,i}^b)$, where one observes that the sum terms are antisymmetric and thus the sum is null, verifying Eq. (67).

Thus, the compatibility Eqs. (31)–(33) are verified by the mixing rule Eq. (59), and we note that this mixing rule is obtained for arbitrary ϕ_i^T, ϕ_i^p, and ϕ_i^k.

2. Mass diffusion

Mixing rules for D^M are determined from the compatibility conditions Eqs. (34)–(36). The point of departure for this derivation is to find if there are constraints on the arbitrary functions ϕ_i^T, ϕ_i^p, ϕ_i^k, and ψ_i that will enable Eqs. (34)–(36) to be satisfied. Rewriting Eq. (28) as

$$X_j D_{p,j} = \sum_{k=1}^{N} D_{jk}^M X_k \tag{68}$$

and using Eq. (68) with Eqs. (35) and (36) implies

$$\psi_i = \frac{m_i}{m}, \tag{69}$$

$$\phi_i^p = \sum_{k=1}^{N} X_k \phi_i^k, \tag{70}$$

which defines ψ_i and constrains ϕ_i^p and ϕ_i^k. A constraint can also be obtained for ϕ_i^T by invoking a relationship obtained from Eq. (57),

$$X_j D_{T,j} = -\sum_{k=1}^{N} D_{jk}^M X_k \overline{\alpha}_{T,k}^b \tag{71}$$

which along with Eqs. (34), (36), and the definition of ϕ_j'

$$\phi_j' \equiv \sum_{k=1}^{N} X_k \overline{\alpha}_{T,k}^b \phi_j^k - \phi_j^T \tag{72}$$

used in combination with Eqs. (71), (34), and (36) results in

$$\sum_{j=1}^{N} K_{ij}^{MQ} (\phi_j' + w_j^T) = \overline{D}_i \left(\overline{\alpha}_{T,i}^b - \frac{m_i}{m} \sum_{k=1}^{N} X_k \overline{\alpha}_{T,k}^b \right) \tag{73}$$

since $\Sigma_{k=1}^N (K^{QQ})_{jk}^{-1} \lambda_k = n R_u w_j^T$ as a result of Eqs. (50) and (55). Also, it may be shown that combining Eqs. (50), (52), and (55) one obtains $\Sigma_{j=1}^N K_{ij}^{MQ} w_j^T = \overline{D}_i \overline{\alpha}_{T,i}^b$ and this along with $\Sigma_{k=1}^N X_k \overline{\alpha}_{T,k}^b = 0$ obtained from Eq. (52) means that ϕ_j' may be taken null. Thus, Eq. (72) provides a direct relationship between ϕ_j^T and ϕ_j^k.

Finding the mixing rules for D^M has now been reduced to determining ϕ_j^k and D_{jk}^M from Eq. (36) as functions of the KT defined properties. Forming G defined by Eq. (37) gives for $i \neq j$, $G_{ij} = -(1 - \Delta_{ij}') \overline{D}_i X_j / D_{ij}$, where Δ' is a symmetric matrix of $O(\|\zeta\|^2)$ that quantifies the coupling between mass and heat fluxes. The rather complex algebraic form of Δ_{ij}' is presented in Appendix A. Furthermore, consonant with the form of Eq. (36), ϕ_j^k is taken as $\beta D_{jk}^M (m_j / X_j)$, where β is an arbitrary multiplier. Thus, collecting all terms proportional to D_{jk}^M in Eq. (36) leads to a correction factor $\Delta_{ij} \equiv \Delta_{ij}' - \beta \zeta_{ij}'$, where $\zeta_{ij}' \equiv m_i m_j \zeta_{ij} / (m_i + m_j)$ and ζ_{ij} is defined by Eq. (4). Using this factor, the first approximation[10] to the binary diffusion coefficient, D_{ij}, is corrected to the full approximation, $\mathcal{D}_{ij}^b$, given by the 13-moment method

$$\mathcal{D}_{ij}^b \equiv \frac{D_{ij}}{(1 - \Delta_{ij})} \tag{74}$$

which further averaged using Blanc's law yields

$$\overline{\mathcal{D}}_i^b \equiv \left(\sum_{j \neq i}^{N} \frac{X_j}{\mathcal{D}_{ij}^b} \right)^{-1} = \frac{\overline{D}_i}{(1 - \overline{\Delta}_i)}, \tag{75}$$

where

$$\overline{\Delta}_i = \overline{D}_i \sum_{j \neq i}^{N} X_j \frac{\Delta_{ij}}{D_{ij}}. \tag{76}$$

The value of β is found by requiring that the correction be minimal; thus minimizing $\|\Delta_{ij}\|$ gives

$$\beta = \frac{\Sigma_{i,j=1}^N (1 - \delta_{ij}) \Delta_{ij}' \zeta_{ij}'}{\Sigma_{i,j=1}^N (1 - \delta_{ij}) (\zeta_{ij}')^2} \tag{77}$$

leading to

$$\phi_j^p = \beta m_j D_{p,j}, \quad \phi_j^T = -\beta m_j D_{T,j}, \tag{78}$$

which now determine the previously arbitrary functions ϕ_j^p and ϕ_j^T.

These definitions of $\mathcal{D}_{ij}^b$ and $\overline{\mathcal{D}}_i^b$ replaced in Eq. (36) result in a singular equation

$$\sum_{j=1}^{N} \left[\delta_{ij} - (1 - \delta_{ij}) X_j \frac{\overline{\mathcal{D}}_i^b}{\mathcal{D}_{ij}^b} \right] \frac{D_{jk}^M}{X_j} = \overline{\mathcal{D}}_i^b \frac{\delta_{ik} - Y_i}{X_i} \tag{79}$$

which is the mixing rule for D^M when combined with the physical constraint $\Sigma_{i=1}^N m_i D_{ij}^M = 0$ that the sum of all mass fluxes must be null and the mathematical constraint $\Sigma_{i=1}^N D_{ij}^M Y_j = 0$. The mixing rule is given in terms of mole or mass fractions and the binary diffusivity matrix $\mathcal{D}_{ij}^b$.

VI. DISCUSSION

A. Final equations

The final transport equations compatible with the 13-moment method are listed below

$$\mathbf{J}_i = -n \left[X_i (D_{T,i} \nabla \ln T + D_{p,i} \nabla \ln p) + \sum_{k=1}^{N-1} \mathcal{D}_{ik} \nabla X_k \right], \tag{80}$$

$$\mathbf{q} = \mathbf{q}'' + \sum_{i=1}^{N} h_i \mathbf{J}_i = -\lambda \nabla T + \sum_{i=1}^{N} (h_i - R_u T \overline{\alpha}_{T,i}^b) \mathbf{J}_i, \tag{81}$$

where $\mathbf{q}$ is the Irwing–Kirkwood (IK) total mixture heat flux,[1,14]

$$D_{T,i} = -\sum_{j=1}^{N} \overline{\alpha}_{T,j}^b D_{ji}^M, \tag{82}$$

$$D_{p,i} = \frac{p}{R_u T} \sum_{j=1}^{N} v_j D_{ji}^M, \tag{83}$$

$$\mathcal{D}_{ik} = \sum_{j=1}^{N} D_{ij}^M \alpha_{D,jk}, \tag{84}$$

$$\overline{\alpha}_{T,i}^b = \sum_{j=1}^{N} X_j \alpha_{T,ji}^b, \tag{85}$$

where $h_i = \mu_i - T(\partial \mu_i / \partial T) = (\partial h / \partial X_i)$ is the molar enthalpy, $\alpha_{T,ij}^b$ is the binary form of the thermal diffusion factor given by Eq. (54), and D^M is determined from the binary diffusivities $\mathcal{D}_{ij}^b$ through Eq. (79).

A more revealing form of Eq. (81) can be obtained using the IK form of the thermal diffusion factor defined by[1]

$$\alpha'_{T,ij}=\alpha^b_{T,ij}+\alpha^h_{T,ij}, \tag{86}$$

where

$$\alpha^h_{T,ij}\equiv\frac{m_i m_j}{mR_uT}\left(\frac{h_i}{m_i}-\frac{h_j}{m_j}\right), \tag{87}$$

which yields

$$\overline{\alpha'}_{T,j}=\sum_{i=1}^{N} X_i\alpha'_{T,ij}=\overline{\alpha}^b_{T,j}+\frac{1}{R_uT}\left(\frac{m_j}{m}h-h_j\right). \tag{88}$$

Using the Eq. (88) form of the thermal diffusion ratios, Eq. (81) can be rewritten as

$$\mathbf{q}=-\lambda\nabla T-R_uT\sum_{i=1}^{N}\overline{\alpha'}_{T,i}\mathbf{J}_i, \tag{89}$$

where the term containing the $\overline{\alpha'}_{T,i}$'s describes the total Dufour effect. Equation (86) shows that if $|\alpha^h_{T,ij}|\gg|\alpha^b_{T,ij}|$, the inaccuracies in $\alpha^b_{T,ij}$ are unimportant in calculating the heat flux.

B. Comparisons with existing derivations

A discussion of mass diffusion mixing rules as relevant to NEQT has been presented by Curtis and Bird[4] from the point of view of the Chapman–Enskog KT. Their approach is to assume the form of the matrix defining the mass diffusion mixing rules and to make arguments that this form is unique; a detailed description of thermal diffusion, which is a major feature of the present investigation is not given in Curtis and Bird.[4] To compare with Curtis and Bird,[4] a nonsingular form of Eq. (79) may be formed

$$\sum_{k=1}^{N-1} M_{ik}D^M_{kj}=\delta_{ij}-Y_i, \tag{90}$$

where

$$M_{ik}=H_{ik}-\frac{m_k}{m_N}H_{iN}, \tag{91}$$

$$H_{ik}\equiv\frac{\delta_{ik}}{\overline{\mathcal{D}}^b_i}-(1-\delta_{ik})\frac{X_i}{\mathcal{D}^b_{ik}} \tag{92}$$

and realize that the relationship between their coefficients $\tilde{D}_{ij}$ and $\tilde{C}_{ij}$ and our coefficients D^M_{ij} and H_{ij} is

$$D^M_{ij}=X_i\tilde{D}_{ij}\quad\text{and}\quad H_{ik}X_k=-\tilde{C}_{ik}. \tag{93}$$

Hence Eq. (4.1) from Curtis and Bird[4] corresponds to our Eq. (90). Therefore, an inversion of Eq. (90) for $N=2$, 3 or 4 may be obtained from Table I of Curtis and Bird.[4] To further compare our presentation with that of Curtis and Bird,[4] we note that the Maxwell–Stefan diffusivities mentioned there are here given by the corrected binary diffusivities, $\mathcal{D}^b_{ij}$, which are valid beyond the first order approximation of Chapman and Cowling.[10] For practical purposes, Δ_{ij} are very small (especially if $T^*\leqslant 1$) and uncertainties in the binary diffusion coefficients imply that the distinction between D_{ij} and $\mathcal{D}^b_{ij}$ may be ignored.

Ern and Giovangigli[6] have proposed a truncated series as an approximate inversion of Eq. (79). This approximation may be written as

$$D^M_{ij}\simeq X_iD^{(1)}_{ij}, \tag{94}$$

where

$$D^{(1)}_{ij}=\frac{(1+Y_i)}{X_i}\mathcal{D}^*_i\delta_{ij}+(1-\delta_{ij})\frac{\mathcal{D}^*_i\mathcal{D}^*_j}{\mathcal{D}^b_{ij}}-(\sigma_i\mathcal{D}^*_i+\sigma_j\mathcal{D}^*_j)+\sum_{k=1}^{N}(Y_k\sigma_k\mathcal{D}^*_k), \tag{95}$$

$$\mathcal{D}^*_i\equiv(1-Y_i)\overline{\mathcal{D}}^b_i, \tag{96}$$

$$\sigma_i=\frac{m_i}{m}(1+Y_i)+\sum_{j\neq i}^{N}Y_j\frac{\mathcal{D}^*_j}{\mathcal{D}^b_{ij}}. \tag{97}$$

Equations (94)–(97) were here tested for several sets of species taken from the list: H_2, He, N_2, O_2, CO_2, H_2O and alkanes for carbon number 1–20. For each set, a total of 10^4 random samples of species mole fraction distributions were taken for $p=1$ atm and $T=300$ K, 600 K, and 1200 K. Binary diffusivities were estimated from a corresponding states formula.[15] Sets of 3–20 species were considered. For each sample, an average signed error and error standard deviation were calculated over N^2 elements of the diffusion matrix D^M, each error being calculated relative to the element magnitude to which the absolute matrix norm multiplied by 0.01 was added in order to account for possible large relative errors for very small elements. Then, averages and extrema were found for all samples. To summarize the results, the average error from the approximate calculation proposed by Ern and Giovangigli[6] to an exact calculation using Eq. (90) was found to be approximately 1% or less; the maximum error was 5%. The overall standard deviation was also approximately 1% or less, with a maximum of 14%. Large errors were found for cases where the mixture contained a combination of very light species (i.e., H_2 or He) and several light (e.g., N_2, CO_2, H_2O, CH_4) species.

C. Applications

Beside the academic interest of mixing rules lie a very large number of practical applications where one must calculate the local composition of a mixture and where transport coefficients must be used in this calculation. However, while KT is extremely useful as a platform to determine structural dependencies, it is less useful in producing accurate transport coefficient values due to algebraic complexity and lack of accuracy of the collision integrals. This is especially true for polyatomic molecules with internal degrees of freedom that substantially alter energy conservation details during collisions and which are not considered in the 13-moment method. This effect is small for mass diffusivities and the shear viscosity, but not so small for the thermal conductivity and bulk viscosity;[13] for example, we conclude that the Ern and Giovangigli[6] approximation is adequate for practical calculations since the uncertainty in empirical binary diffusivities is approximately 1% or larger.[15] Various semiempirical

methods, most notably the method of corresponding states, are commonly used to estimate properties such as viscosity, thermal conductivity, enthalpies, heat capacities and also binary diffusion coefficients.[7,15]

Some practical calculations of thermal diffusion effects are presented in the literature[2,3,5,6] where it is noted that for BK thermal diffusion factors, internal energy effects may be considered intermediate in importance. Ern and Giovangigli[6] consider internal degrees of freedom in their matrix Λ_{ij} which would correspond to our expression $(5/2)X_iK_{ij}^{QQ}/(\mathrm{Le}_i\,\underline{D}_i)$; comparison of our expression to theirs shows that their inclusion of internal degrees of freedom in Le_i and $\varkappa_{ij}$ would result in modifications of the weighting factors w_i^Q and w_i^T. These weighting factors may thus be available either through calculations using expressions including internal degrees of freedom effects or through semiempirical means.

The same species and temperatures used to test the accuracy of the approximate inversion found in Ern and Giovangigli[6] were here adopted for a set of tests performed to determine the behavior of the U series given by Eq. (47). The value of $\varkappa_{ij}$ was taken as 2.4, consistent with values mentioned earlier in conjunction with the Lennard-Jones potentials. For a chosen value of Le_i, the matrix U was first calculated through an exact inversion and then through a series expansion as given by Eq. (47). For each Le_i, the results from the series expansion were compared to the value calculated through matrix inversion. The typical number of terms to obtain an error of $O(10^{-2})$ was 3, 6 and 12–15 for Le_i of 0.5, 1.0, and 1.5, respectively. Thus, the use of this series in KT to find values of w_i^Q and w_i^T is practical only for $\mathrm{Le}_i \lesssim 1$.

D. Calculations for high pressure conditions

The mixing rules developed here are expected to be rigorously valid as long as binary molecular interactions dominate, that is, for the reduced density, $\rho_r \equiv \rho/\rho_c \lesssim 0.1$, where the subscript c denotes the critical point. For $\rho_r = O(1)$, rigorous and accurate simulations of multicomponent mixtures may be in principle obtained using molecular dynamics computations. However, such simulations are currently in a state of infancy.[16–19]

For high pressure calculations, there are two questions that must be answered: Is the structure of the mixing rules obtained here still valid? Are the $\mathcal{D}_{ij}^b$, $\alpha_{T,ij}^b$, and Le_i possible to obtain either by semiempirical methods or calculations?

1. Mass diffusion

Curtis and Bird[4] noted that the BK KT of monoatomic liquid mixture proposed by Bearman and Kirkwood[20] and Bearman[21] gives Maxwell–Stefan flux relations that parallel those of dilute gas KT if the corresponding Maxwell–Stefan diffusivities are $D_{ij}^{M-S} = kT/(n\gamma_{ij})$, where the γ_{ij} are friction coefficients. These friction coefficients account for molecular interactions.[4] Taking this relationship a step further, if γ_{ij} are proportional to the corresponding binary viscosities, then the commonly used Stokes–Einstein form for liquid diffusivity is obtained. Although this is only suggestive, it permits considering an extension of the current mass diffusion mixing rules, that is Eq. (79), to high densities, provided that proper binary mass diffusion coefficients are employed; the calculation of high density mass diffusion coefficients is discussed by Harstad and Bellan.[15] Empirical evidence for the use of the Maxwell–Stefan flux relations for dense gases and liquids is also cited by Hirshfelder *et al.*[13]

2. Thermal diffusion

Assuming that the current linear structure of the thermal diffusion factor mixing rule, Eq. (59), is valid, one needs to know $\overline{\alpha}_{T,i}^b$ which are calculated from the $\alpha_{T,ij}^b$ through Eq. (85). At high p, reliable expressions to perform such calculations are not readily available. At low p, calculations of $\overline{\alpha}_{T,i}^b$ are available[2,3,5,6] based on KT and semiempirical means. If one postulates that these calculations hold at high p, then the necessary information as input to these calculations are $\mathrm{Sc}_i = \mathrm{Pr}_i\,\mathrm{Le}_i$, where Sc_i and Pr_i are the species Schmidt and Prandtl numbers.

The lack of information on thermal diffusion factors in high density mixtures means that departures from the linear mixing rules are unknown. Some estimates of binary thermal diffusion factors for hydrocarbons at pressures of 1 atm to 56 atm, made using what is known as ''thermodynamic models,'' are evaluated in Gonzales-Bagnoli *et al.*;[22] the various forms of this type of model give inconsistent and often poor results when compared to the sparse available data, so that considerable caution in their use is advised. Estimates of high ρ_r BK binary thermal diffusion factors remain problematic, with one indication of a strong ρ_r dependence.[18]

E. Present contribution

Existing mixing rules, which have been derived from KT, are inherently valid only for the perfect gas equation of state, that is for $\alpha_{D,ij} = \delta_{ij} - \delta_{iN}$. In contrast, the present mixing rules, Eqs. (59) and (79), used along with the transport Equations (80)–(85), are valid for any equation of state. Thus, these mixing rules form the basis for modeling fluids under very general conditions (except around the critical locus, where additional considerations are required). These equations enable the utilization of estimates, beyond the KT formalism, of transport properties based on binary molecular interaction. Current information suggests that the mass diffusion mixing rules derived here may still be valid at high pressure, although this still needs to be further ascertained. Whereas the current state of knowledge does not allow projecting the validity of the linear thermal diffusion mixing rules derived here to high pressure conditions, the lack of any other information implies that there may not be any other choice but using them, and trying to devise experiments where they could be indirectly assessed.

ACKNOWLEDGMENTS

This work was conducted at the Jet Propulsion Laboratory (JPL), California Institute of Technology (Caltech) and sponsored by the National Aeronautics and Space Administration (NASA) Microgravity Combustion program with Dr. Merrill King as contract monitor and Dr. Chih-Jen Sung as technical contact with the National Center for Microgravity Research on Fluids and Combustion.

APPENDIX A: DEPENDENCIES OF RELEVANT PARAMETERS ON COLLISION INTEGRALS

From KT,

$$(\mathrm{Le}_i)^{-1}=\overline{D}_i\left\{\frac{4}{5}A_{ii}^*\frac{X_i}{D_{ii}}+\sum_{j\neq i}\frac{X_j}{D_{ij}(m_i+m_j)^2}\times\left[3m_i^2+\frac{8}{5}A_{ij}^*m_im_j+\left(\frac{5}{2}-\frac{6}{5}B_{ij}^*\right)m_j^2\right]\right\}. \tag{A1}$$

The cross-coupling matrix is

$$\begin{aligned}\Delta'_{ij}=\Delta'_{ji}=\frac{5}{2}\Bigg\{&\frac{(\Lambda_i\zeta_i^*m_j+\Lambda_j\zeta_j^*m_i)\zeta_{ij}}{m_i+m_j}-\frac{1}{2}\zeta_i^*\zeta_j^*D_{ij}\left(\frac{\Lambda_i}{D_{ij}^Q}+\frac{\Lambda_j}{D_{ji}^Q}\right)+D_{ij}\sum_{k\neq i,j}w_k\left[\frac{\Lambda_i\zeta_i^*}{D_{ik}^Q}\frac{m_j\zeta_{jk}}{(m_j+m_k)D_{jk}}+\frac{\Lambda_j\zeta_j^*}{D_{jk}^Q}\frac{m_i\zeta_{ik}}{(m_i+m_k)D_{ik}}\right]\\&-D_{ij}\left[\sum_{k\neq i,j}\Lambda_kw_k\frac{m_im_j\zeta_{ik}\zeta_{jk}}{(m_i+m_k)(m_j+m_k)D_{ik}D_{jk}}+\frac{1}{2}\sum_{k\neq i}\sum_{m\neq j}\left(\frac{\Lambda_k}{D_{km}^Q}+\frac{\Lambda_m}{D_{mk}^Q}\right)\times w_kw_m\frac{m_im_j\zeta_{ik}\zeta_{jm}}{(m_i+m_k)(m_j+m_m)D_{ik}D_{jm}}\right]\Bigg\},\end{aligned} \tag{A2}$$

where

$$\zeta_i^*\equiv\mathrm{Le}_i\,\overline{D}_i\sum_{j\neq i}\frac{m_jX_j}{m_i+m_j}\frac{\zeta_{ij}}{D_{ij}}. \tag{A3}$$

APPENDIX B: BINARY AND TERNARY DIFFUSION COEFFICIENTS AND THERMAL DIFFUSION FACTORS

For $N=2$,

$$D_{m,12}=\mathcal{D}_{12}^b,\quad \overline{D}_1=\frac{D_{12}}{X_2}, \tag{B1}$$

$$(D_{12}^Q)^{-1}=\frac{\varkappa'_{12}}{D_{12}}, \tag{B2}$$

$$\frac{1}{\Lambda_1}=\frac{1}{\Lambda_2}=1-\mathrm{Le}_1\,\mathrm{Le}_2(\varkappa'_{12})^2, \tag{B3}$$

$$w_1^Q=\left(1+\mathrm{Le}_2\,\varkappa'_{12}\frac{X_2}{X_1}\right)\Lambda_1. \tag{B4}$$

For $N=3$,

$$D_{m,12}=\frac{m}{m_1m_2\Delta_3^M}\left[\frac{m_1(1-Y_1)}{\mathcal{D}_{23}^b}+\frac{m_2(1-Y_2)}{\mathcal{D}_{13}^b}-\frac{m_3Y_3}{\mathcal{D}_{12}^b}\right], \tag{B5}$$

where

$$\Delta_3^M=\frac{X_1}{\mathcal{D}_{12}^b\mathcal{D}_{13}^b}+\frac{X_2}{\mathcal{D}_{12}^b\mathcal{D}_{23}^b}+\frac{X_3}{\mathcal{D}_{13}^b\mathcal{D}_{23}^b}, \tag{B6}$$

$$\frac{\Lambda_1}{D_{12}^Q}=\frac{1}{\Delta_3^Q}\left(\frac{\varkappa'_{12}}{D_{12}}+w_3\frac{\varkappa'_{13}}{D_{13}}\frac{\varkappa'_{23}}{D_{23}}\right), \tag{B7}$$

$$\Lambda_1=\frac{1}{\Delta_3^Q}\left[1-w_2w_3\left(\frac{\varkappa'_{23}}{D_{23}}\right)^2\right], \tag{B8}$$

$$w_1^Q=\frac{1}{\Delta_3^Q}\left[1+w_2\frac{\varkappa'_{12}}{D_{12}}+w_3\frac{\varkappa'_{13}}{D_{13}}+w_2w_3\frac{\varkappa'_{23}}{D_{23}}\times\left(\frac{\varkappa'_{12}}{D_{12}}+\frac{\varkappa'_{13}}{D_{13}}-\frac{\varkappa'_{23}}{D_{23}}\right)\right], \tag{B9}$$

with

$$\Delta_3^Q=1-\left[w_1w_2\left(\frac{\varkappa'_{12}}{D_{12}}\right)^2+w_1w_3\left(\frac{\varkappa'_{13}}{D_{13}}\right)^2+w_2w_3\left(\frac{\varkappa'_{23}}{D_{23}}\right)^2\right]-2w_1w_2w_3\frac{\varkappa'_{12}}{D_{12}}\frac{\varkappa'_{13}}{D_{13}}\frac{\varkappa'_{23}}{D_{23}}. \tag{B10}$$

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